

due to Varian Associates and Mr. E. Pier for obtaining the 32.1-Mc. B¹¹ n.m.r. spectrum.

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RECEIVED JUNE 6, 1964

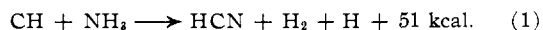
The Reaction of CH Radicals with Ammonia¹

Sir:

The reactions of active nitrogen with hydrocarbons have been carefully studied by Winkler and others² who found that, generally, the major nitrogen-containing product was HCN. Although the quantitative aspects of HCN formation in these reactions have been widely investigated, it is still in doubt whether N atoms are the sole reactive species, or if metastable N₂ molecules play a role.

As a part of his basic investigations of hydrocarbon reactions with active nitrogen, Winkler³ added NH₃ upstream from the C₂H₄ reaction flame. Instead of observing a possible decrease in HCN production, as expected, a slight increase was found. He attributed this increase in HCN production to efficient "poisoning" of the vessel walls against N-atom recombination,⁴ the slightly higher N-atom concentration leading to increased HCN formation.

We also added NH₃ upstream from some hydrocarbon-active nitrogen flames, in experiments analogous to those of Winkler. However, when we added NH₃ upstream from the C₂H₂ reaction flame (pressure ~0.25 mm. and linear velocity ~10 m./sec.), NH₃ was substantially consumed and H₂ and HCN were produced (in addition to that formed without NH₃).⁵ Without NH₃ about 10% of the N atoms present (as measured by titration with NO)^{6,7} formed HCN. Upon addition of NH₃, the formation of HCN increased by about 50% while the equivalent amount of NH₃ was consumed. In addition, sufficient H₂ was produced to suggest the following reaction.



The products were analyzed by means of a CEC 21-130 mass spectrometer whose leak was located just below the flame zone. In order to confirm our experimental results, the study of this reaction was repeated in another system, at pressures of about 1 mm., using a Bendix Model 12 time-of-flight mass spectrometer for the analyses; the same increase of HCN was found.

(1) The research reported in this document has been sponsored in part by the Air Force Office of Scientific Research under Grant No. AF-AFOSR-174-63 and in part by the National Aeronautics and Space Administration under NSG-100-60 and NSG-158-61.

(2) References for these studies are too numerous to list here; however, see, for example, H. G. Evans, G. R. Freeman, and C. A. Winkler, *Can. J. Chem.*, **34**, 1271 (1956).

(3) C. A. Winkler and H. I. Schiff, final report to the Geophysics Research Directorate, Air Force, Cambridge Research Laboratories, Bedford, Mass., Project 4984. ARPA 42, under Contract No. AF19(604)-5979, May, 1962, p. 26.

(4) See ref. 3, p. 40.

(5) As a point of interest, we would like to mention that we were able to produce a stream of metastable N₂(A²Σ_u⁺) molecules by means of surface-catalyzed excitation (to be published) and found that, surprisingly, no decomposition of NH₃, or formation of H₂, was observed when NH₃ was added to this stream.

(6) G. B. Kistiakowsky and G. G. Volpi, *J. Chem. Phys.*, **27**, 1141 (1957).

(7) P. Harteck, R. R. Reeves, and G. Mannella, *ibid.*, **29**, 608 (1958).

An estimate of the rate of reaction, calculated from the length of the flame zone and the corresponding time of reaction, shows that the consumption of NH₃ is quite fast and that the specific rate coefficient must be at least $k_1 = 10^{-13}$ cc./particle sec.) for the above reaction.

If reaction 1 is actually responsible for the increased HCN formation, it should be possible to react NH₃ with CH radicals in the absence of N atoms. It is known that CH radicals are produced in the reactions of hydrocarbons with O atoms⁸ and, under favorable conditions, H atoms also react with hydrocarbons giving small amounts of CH radicals.⁸ Therefore, CH radicals were produced by reacting O or H atoms with C₂H₂, and addition of NH₃ to the flame zones of these reactions resulted in the production of HCN in the absence of N atoms. These findings strongly support the proposed consumption of NH₃ and formation of HCN by reaction 1. Without hydrocarbons present, at our low pressures and high pumping velocity, NH₃ was not attacked by either N or H atoms, and only slightly by O atoms.

Alternative reactions of NH₃ with C₂H, CH₂, CH₃, and other radicals have been considered, but all of these appear unlikely because of energetic, geometric, or spin considerations.

(8) A. G. Gaydon, "Spectroscopy of Flames," Chapman and Hall, London, 1957, p. 252.

(9) This paper is taken in part from a thesis by D. R. Safrany submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, in the Department of Chemistry, at Rensselaer Polytechnic Institute.

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RECEIVED MAY 27, 1964

Optical Rotatory Dispersion of Carbohydrates¹

Sir:

The study of optical rotatory dispersion has recently been facilitated by the commercial availability of instruments capable of continuously measuring the optical rotation down to 185 mμ. This communication reports studies on the rotatory dispersion of several simple sugars and derivatives thereof, measured on a Cary Model 60 recording spectropolarimeter. The study was initiated to see if information relating to the conformation of carbohydrates in solution could be obtained from such measurements.

Figure 1 shows dispersion curves for D-glucose and D-sorbitol. It is seen that no Cotton effect is visible down to 190 mμ. This result is consistent with ultraviolet absorption data, which show no absorption peaks in this region.² An earlier report by Foster and Rao³ that glucose and sorbitol exhibit Cotton effects near 220 mμ appears to be in error.⁴

Curves of an identical nature but of different rotational magnitudes were also obtained for D-allose,⁵ D-mannose, 2-amino-2-deoxy-D-glucose, 2-deoxy-D-glucose, L-rhamnose, D-glucose 6-phosphate, α-D-glucosyl

(1) This work was supported by grants A 2903(C-5) and AM-04576 from the National Institutes of Health, U. S. Public Health Service.

(2) G. O. Phillips and P. Barber, *J. Chem. Soc.*, 3990 (1963).

(3) V. S. R. Rao and J. F. Foster, *Nature*, **200**, 570 (1963).

(4) J. F. Foster (personal communication) has confirmed the absence of Cotton effects for these compounds.

(5) We are indebted to Dr. N. K. Richtmeyer of the National Institutes of Health for this material.